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## SCIENCE OF LIGHT

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## A Double Beam, Double and Multiple Pass Infrared Spectrophotometer

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(Received February 1, 1956)

An experimental infrared spectrophotometer of double beam, double and multiple pass type has been constructed by installing two small plane mirrors at right angle to each other between Walsh mirrors, and 10.5  $\mu$  band of ammonia is satisfactorily recorded.

### 1. Introduction

The double and multiple monochromator invented by A. Walsh<sup>1)</sup> not only gives excellent resolution but also makes the effect of scattered light small enough to be negligible. These two features are important for a spectrometer. However, with a single beam type, which has a long optical path, spectrum is strongly disturbed by atmospheric absorption lines. In order to eliminate this disturbance, the instrument would have to be operated in vacuum which would be very troublesome and expensive. In the case of a double beam type, the atmospheric lines have no effect, and at the same time the percentage of absorption is directly obtained. Therefore, the double beam system of double and multiple pass type is highly desirable. For the realization of such instrument, various methods<sup>2)-4)</sup> are considered possible for which the following requirements should be kept in mind.

- a) A good use of the merits of Walsh's monochromator to be made.
- b) Energy loss to be made minimum.
- c) Simplicity of optical arrangement.

The author devised a double beam type which can fulfill all of the above requirements by installing two small plane mirrors at right angle to each other between Walsh mirrors, and obtained recording by an experimental set of double pass type.

- 1) A. Walsh: *Nature*. **167** (1951) 810.  
A. Walsh: *J. Opt. Soc. Amer.* **42** (1952) 94.  
N. S. Ham, A. Walsh and J. B. Wills: *Nature*. **169** (1952) 977.  
N. S. Ham, A. Walsh and J. B. Wills: *J. Opt. Soc. Amer.* **42** (1952) 496.
- 2) A. Walsh: *J. Opt. Soc. Amer.* **43** (1953) 215.
- 3) A. R. H. Cole: *J. Opt. Soc. Amer.* **43** (1953) 807.
- 4) S. F. D. Orr: *J. Opt. Soc. Amer.* **43** (1953) 709.
- 5) J. Pliva: *Jl. Sci. Instrum.* **31** (1954) 434.

The purpose of this paper is not to examine resolution of a double beam, bouble and multiple pass infrared spectrophotometer, but to verify the capability of recording by means of the new optical system.

## 2. Optical system

The optical system is shown in Fig. 1. Arrangement in monochromator is the same as that<sup>6)</sup> of the single beam double pass infrared spectrometer already published except that a new mirror system is attached in the neighbourhood of Walsh mirrors as shown enlarged Fig. 2. Once dispersed spectrum by prism  $P$  is reflected by Walsh mirror  $M_6$  and a plane mirror  $M_7$ , and goes out of the monochromator into a double beam system by a semi-circular plane mirror  $M_8$  with chopping frequency 5 c.p.s. and plane mirror  $M_8'$  concave mirrors  $M_9$  and  $M_9'$ . Finally, it enters again into the monochromator by plane mirror  $M_{10}$  and Walsh mirror  $M_{11}$ . Two faces of a slender right angle prism are actually used instead of the plane mirrors  $M_7$  and  $M_{10}$ . Sample cell  $C$  is placed between  $M_6$  and  $M_{10}$ , and in front of  $M_8'$  attenuator  $W$  is set. The image of entrance slit  $S_1$  is formed on fixed slits  $S_3$  and  $S_4$  shown in Fig. 2, and if the right angle

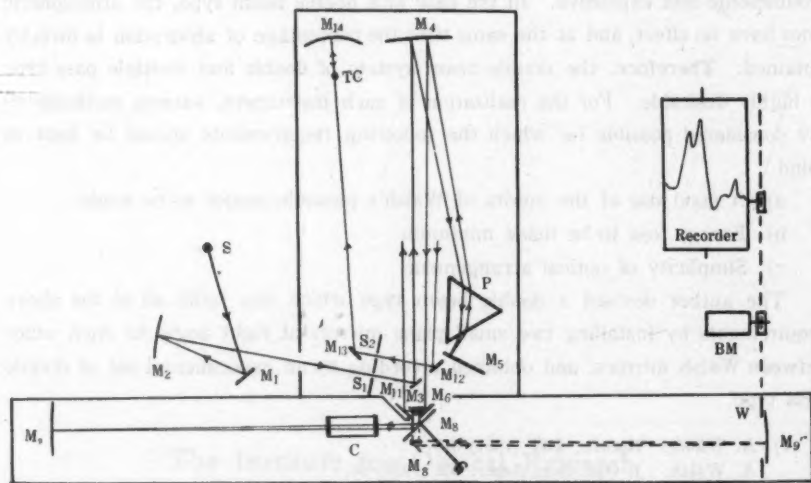


Fig. 1. Arrangement of a double beam double pass infrared spectrophotometer.

$S$ , radiation source;  $S_1, S_2$ , entrance and exit slits;  $M_1, M_3, M_5, M_{12}, M_{13}$ , plane mirrors;  $M_4$ , paraboloidal mirror;  $P$ , prism;  $M_6$ , Littrow mirror;  $M_6, M_{11}$ , Walsh mirrors;  $M_8$ , semi-circular plane mirror;  $M_2, M_9$  and  $M_9'$ , concave mirrors;  $M_{14}$ , ellipsoidal mirror;  $TC$ , thermocouple;  $C$ , sample cell;  $W$ , optical wedge;  $BM$ , balancing motor.

6) Keiei Kudo and Tadashi Miyazaki: J. of Applied Physics. Japan, **24** (1955) 461.

prism is removed, the instrument becomes a single beam type. If wider Walsh mirrors  $M_6$  and  $M_{11}$  are used in consideration of the slit curvature, it becomes a double beam multiple pass type.

### 3. Result

It has been recognized that Walsh's double and multiple monochromator gives an excellent resolution. For the present with a set experimentally assembled, it will suffice to see if a true recording of spectrum is attained by this new arrangement. With a slit on hand which is not compensated for twice dispersed spectrum,  $10.5\mu$  band of ammonia was satisfactorily recorded as shown in Fig. 3 using a fixed slit width.

The author is contemplating to examine the resolution and the effect of scattered light with an instrument properly constructed.

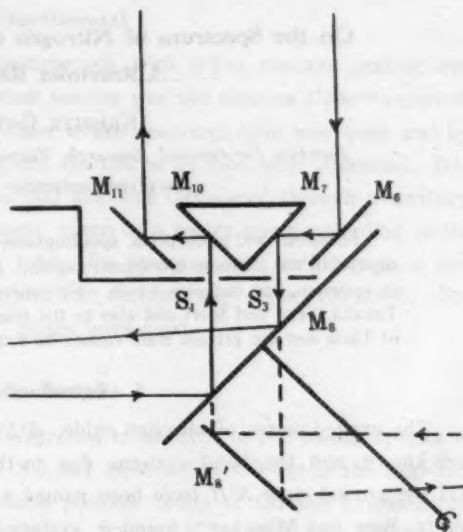


Fig. 2. Arrangement in the neighbourhood of Walsh mirrors.

Plane mirrors  $M_7$  and  $M_{10}$  at right angle to each other are placed between Walsh mirrors  $M_6$  and  $M_{11}$ .

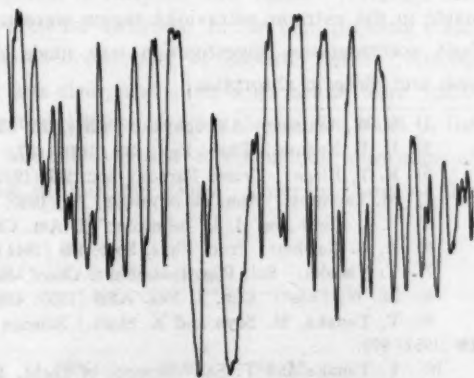


Fig. 3. Ammonia  $10.5\mu$  band recorded by an experimental set of double beam, double pass infrared spectrophotometer.

## On the Spectrum of Nitrogen Oxide in the Extreme Ultraviolet Region

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(Received September 6, 1955)

Emission and absorption spectrograms of nitrogen oxide are investigated in the extreme ultraviolet region.  $E^2\Sigma^+ - X^2\Pi$  system are found in emission, but emission bands which correspond to  $F_2$ ,  $E_3$ ,  $E_4$  bands of Tanaka, Seya and Mori and also to the transitions between  $S$ ,  $T$ ,  $U$ ,  $V$ ,  $W$  of Ueda and the ground state cannot be found.

### 1. Introduction

The excited states of nitrogen oxide,  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Sigma$ ,  $D^2\Sigma^+$  and  $E^2\Sigma^+$  are well-known, and the band systems due to the transitions between these states and the ground state  $X^2\Pi$  have been named  $\gamma$ ,  $\beta$ ,  $\delta$ ,  $\epsilon$  and  $\gamma'$  systems.<sup>1)-11)</sup> Recently, Baer and Miescher<sup>12)</sup> found  $\beta'$  system in the extreme ultraviolet emission and Miescher<sup>13)</sup> confirmed by the rotational analysis that  $\beta'$  system is due to the transition between new  $B$  and the ground state. Further, by the vibrational analysis in the extreme ultraviolet region, Tanaka<sup>14)</sup> found  $\beta''$  system in emission and Ueda<sup>15)</sup> found  $S$ ,  $T$ ,  $U$ ,  $V$ , and  $W$  progressions in absorption.

In this work, photographs of emission and absorption spectra of nitrogen oxide in the extreme ultraviolet region were taken, and by the comparison of both spectrograms, investigation was made on the newly found bands in emission and those in absorption.

- 1) S. W. Leifson: *Astrophys. J.*, **63** (1926) 73.
- 2) H. P. Knauss: *Phys. Rev.*, **32** (1928) 417.
- 3) R. T. Birge: *Trans. Faraday Soc.* **25** (1929) 707.
- 4) M. Lambrey: *Ann. de physique*, **14** (1930) 95.
- 5) P. J. Flory and H. L. Johnston: *J. Am. Chem. Soc.*, **57** (1935) 2641.
- 6) A. G. Gaydon: *Proc. Phys. Soc.*, **95** (1944) 56, **96** (1944) 160.
- 7) Y. Tanaka: *Sci. Pap. Inst. Phys. Chem. Res.*, **43** (1948) 28.
- 8) M. W. Feast: *Can. J. Res.* **A28** (1950) 488.
- 9) Y. Tanaka, M. Seya and K. Mori: *Science of Light*, **1** (1951) 80 *J. Chem. Phys.*, **19** (1951) 979.
- 10) Y. Tanaka and T. Sai: *Science of Light*, **1** (1951) 85.
- 11) M. Ogawa: *Science of Light*, **3** (1955) 90.
- 12) P. Baer and E. Miescher: *Helv. Phys. Acta*, **24** (1951) 331.
- 13) E. Miescher: *Can. J. Res.* **33** (1955) 355.
- 14) Y. Tanaka: *J. Chem. Phys.*, **21** (1953) 788.
- 15) M. Ueda: *Science of Light*, **3** (1955) 143.

### Experimental

A grazing incidence vacuum spectrograph with a 3 m concave grating was used and the procedure for absorption spectra was the same as Ueda<sup>10</sup> reported.

For emission spectra, II type water cooled discharge tube was used and by a fluorite window the spectrograph and the discharge tube were separated. Into the discharge tube, fresh and dry NO gas was introduced through a capillary and pumped by a mercury diffusion pump or a rotary pump according to the desired pressure in the discharge tube. Its pressure was varied from a few hundredth mmHg to a few mmHg and the current was about 120 mA. For photographic plates, Kodak S.W.R. plates were used.

### 2. Results

On low pressure emission spectrograms, in addition to NO bands, spectra of  $N_2$ , N, O due to the dissociation of NO and spectrum of CO due to the stop-cock grease appeared. Particularly, fourth positive bands of CO and Lyman-Birge-Hopfield bands of  $N_2$  were troublesome. The high pressure emission spectrograms, however, were scarcely contaminated by impurity bands. On absorption spectrograms, fourth positive bands of CO appeared weakly as impurity. Analyzed region was 1950A-1500A.

$E^2\Sigma^+ - X^2\Pi$  system. Not only 0-0, 1-0, 2-0 bands in absorption as in previous work<sup>8)9)10)</sup>, but also  $v'-v''$  system in emission were found. Although this system appeared even in the low pressure emission, in the high pressure emission more bands were found due to no overlapping of impurity bands. Among this system only 0- $v''$  progression was clear, and some other bands were indistinct because of overlapping of rotational lines of other bands, 2-0 band in the high pressure emission was faint, but this was due to continuous absorption of oxygen produced by decomposition of nitrogen oxide. Observed band of this system are shown in Table 1.

Table 1.  $E^2\Sigma^+ - X^2\Pi$  system ( $cm^{-1}$ )

$v' \backslash v''$	0	1	2	
0	60720 60831	58841 58969	56999 57126	55188 55314
1	63091 63195	61215 61331		
2	65359 65500			

$\beta'$  system. For the first time, this system was found as  $B$  progression by Tanaka, Seya and Mori<sup>9)</sup>.

In emission, the bands reported by Tanaka<sup>14)</sup>, and in absorption, those by Ueda<sup>15)</sup> were obtained. Ueda found  $\beta^*$  system with the same structure as  $\beta'$  system. On the author's spectrograms, both in the low pressure emission and in absorption, 1-0, 2-0 bands of  $\beta^*$  system clearly appeared, and in addition 1-1, 2-1, 2-2, 2-3 bands were found in the low pressure emission. In absorption, 0-0 band of  $\beta^*$  system was not clear, and in emission 0- $v''$  progression could not be found. From the facts above mentioned and the intensity distribution, the author provisionally regarded  $\beta^*$  system excepting 0-0 band as the extension of  $\beta'$  system, although  $\Delta G$  anomaly remains yet unexplained. Deslandre's table of  $\beta'$  system, including  $\beta^*$  system excepting 0-0 band is shown in Table 2.

Table 2.  $\beta'$  system ( $\text{cm}^{-1}$ )

$v'' \backslash v'$	0	1	2	3	4
0		58007 (4)	56174 (4)	54351 (4)	52558 (4)
		58158 (4)	56310 (4)	54489 (4)	52897 (4)
1	61075 (4)	59186 (5)	57359 (3)		
	61214 (4)	59325 (5)	57757 (3)		
2	62234 (5)	60347 (7)	58528 (2)	56694 (2)	54897 (4)
	62368 (5)	60492 (7)	58667 (2)	56814 (2)	55035 (4)
3	63346 (7)	61473 (5)			
	63474 (7)	61609 (5)			
4	64470 (7)	62622 (3)			
	64592 (7)	62730 (3)			
5	65504 (5)	63624 (5)	61776 (5)		
	65637 (5)	63754 (5)	61905 (5)	60079 (3)	
6	66470 (3)				

Figures in parentheses show intensities.

Other band systems. For  $\gamma$  system, only 3-0 band appeared in emission and adsorption in this region.

For  $\epsilon$  system, 0-0, 1-0, 2-0, 3-0, 4-0 bands in absorption were found and in emission from  $v'=0$  to  $v'=4$  several bands were found, but 4-0 band was not found probably because of self-absorption. In the low pressure emission some bands of this system were obscured by impurity bands as  $E-X$  system.

For  $\delta$  system, only 0-0 band weakly appeared in emission, but in absorption 0-0, 1-0, 2-0 bands appeared very strongly and their intensities were the greatest of all the bands recorded on the plate.

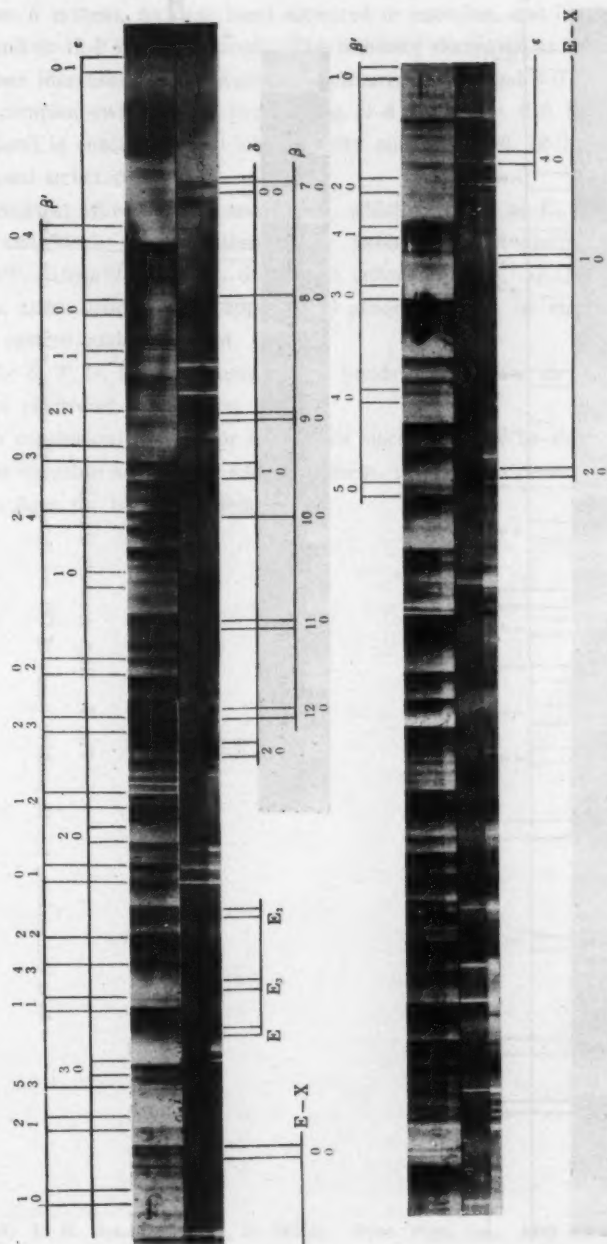


Fig. 1.

Upper: low pressure emission

Lower: absorption

Emission and absorption spectra are taken on the same plate for comparison.

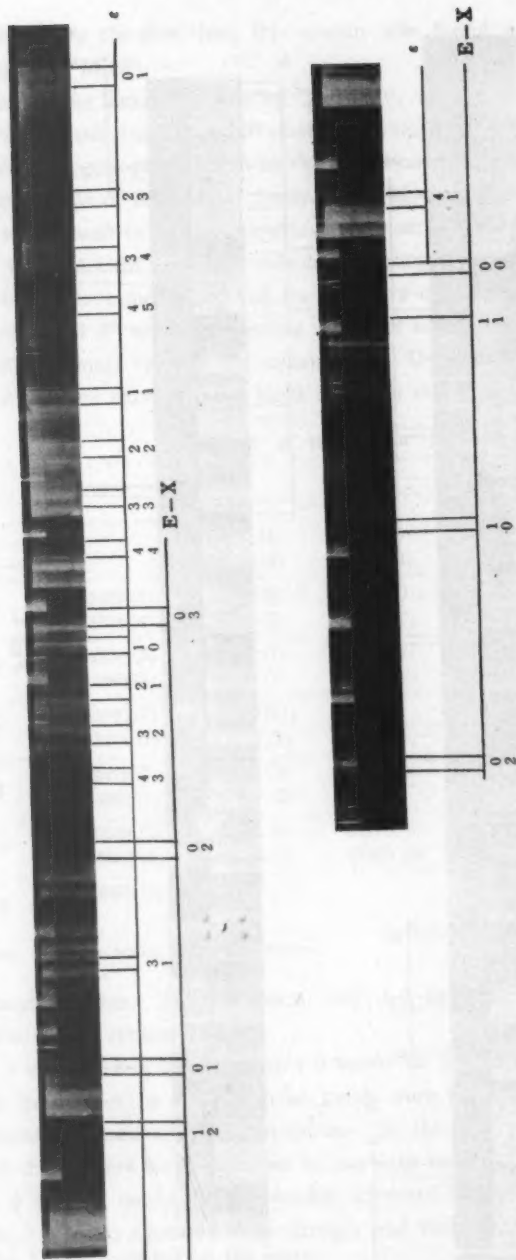


Fig. 2. High pressure emission

As a comparison, fourth positive bands of CO are shown on the upper part of the plate.

For  $\beta$  system, no clear band appeared in emission, and in absorption, from 7-0 band to 12-0 band appeared. The intensity decreases as increases till  $v'=10$  and then increases. The rotational structures of 7-0 and 8-0 bands of  $\beta$  system seem complex owing to the overlapping of  $\delta$  0-0 and  $\epsilon$  0-0 bands respectively, 10-0 band is obscure due to low intensity and 9-0, 11-0, 12-0 bands display clear rotational structures.

Bands at 1676Å, 1688Å and 1768Å, which reported as  $E_1$ ,  $E_2$ ,  $F_2$  by Tanaka, Seya and Mori, were ascribed to the extension of  $\beta$  system by Sutcliffe and Walsh<sup>16)</sup>. Ueda<sup>16)</sup>, however, denied the latter's opinion. In the author's spectrograms, these bands clearly appeared in absorption, but in emission no band of  $v'-v''$  system could be found.

For S, T, U, V, W systems, these bands were found in absorption, but so far not confirmed in emission.

In conclusion, the author wishes his sincere thanks to Prof. Yoshio Fujioka for his valuable advise and encouragement. He is also much indebted to Prof. Masao Seya for his kind guidance.

16) L. H. Sutcliffe and A. D. Walsh: Proc. Phys. Soc., **A66** (1953) 209.

## Infrared Investigation on Mixtures of Acetone and Water

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(Received January 10, 1956)

Infrared absorption spectra of mixtures of acetone and water are recorded in the region from  $1.4\mu$  to  $2\mu$ . As a result, two associational bands, each of which consists of two absorption maxima, are observed in  $1.5\mu$  and  $1.76\mu$  regions. The former is interpreted as corresponding to the  $1.38\mu$  water vapor band shifted by hydrogen bonding, and the latter resulting from simultaneous transition of O-H stretching vibration of water, C-O stretching vibration of acetone and any vibration associated with hydrogen bonding. In addition, for assignment of the  $1.8\mu$  water band a new suggestion is made.

### 1. Introduction

The infrared absorption spectra of mixtures of acetone and water have been studied by D. Williams and E. K. Plyler<sup>1)</sup>. They observed only one band in  $2.7\mu$  region, and stated that "Although it is impossible from the observation of only one absorption band to determine definitely the nature of the mechanism producing it, the authors were inclined toward a belief in the existence of an association compound,...."

With a near infrared grating spectrometer<sup>2)</sup> of a great resolving power, measurements of the absorption spectra of water in acetone were undertaken in detail along a region from  $1.4\mu$  to  $2\mu$ . As a result, two new absorption bands were found in the longer wavelength side of the  $1.45\mu$  band of water, and the evidence<sup>3)</sup> for hydrogen bonding between acetone and water was obtained.

In addition, two new absorption bands arising from the association compound were also observed in  $1.76\mu$  region, and it was concluded that they would likely be related to simultaneous vibrational transition arising from the hydrogen bending.

### 2. Experimental and Results

Acetone was dried for several days over anhydrous potassium carbonate, and distilled: its boiling point was  $56.2-56.6^\circ\text{C}$ . The near infrared spectrometer<sup>2)</sup>

1) D. Williams and E. K. Plyler: *J. Chem. Phys.* **4** (1936) 154.

2) Y. Sakayanagi and Y. Satō: *Science of Light* **33** (1955) 84.

3) Y. Satō and S. Nagakura: *Science of Light* **4** (1955) 120.

used was equipped with a plane grating in conjunction with a PbS photoconductive cell. Calibration of wavelength was made by the use of vibrational-rotational lines of moisture in air. The two absorption cells were used, one of thickness 1.2 mm for use in  $1.51\mu$  region and other of thickness 2 mm for measurements in  $1.76\mu$  region. The absorption spectra were recorded for three mixtures of acetone and water.

The infrared absorption spectra obtained are shown in Figs. 1 and 2, in which indicated numerals close to each curve represent weight-percentages of concentrations of water to acetone.

### 3. Discussions

As can clearly be seen from Fig. 1, with addition of water in acetone, there appear two new absorption bands in the longer wavelength side of the  $1.45\mu$  band of water, and their intensities increase with the increase in concentration of water. Now, the  $1.45\mu$  water band which also consists of two absorption bands\*, is naturally considered as corresponding to the  $1.38\mu$  band of the vapor state, which has been assigned to the combination band  $\nu_1 + \nu_3^{(4)}$ , each of which is the O-H stretching vibration.

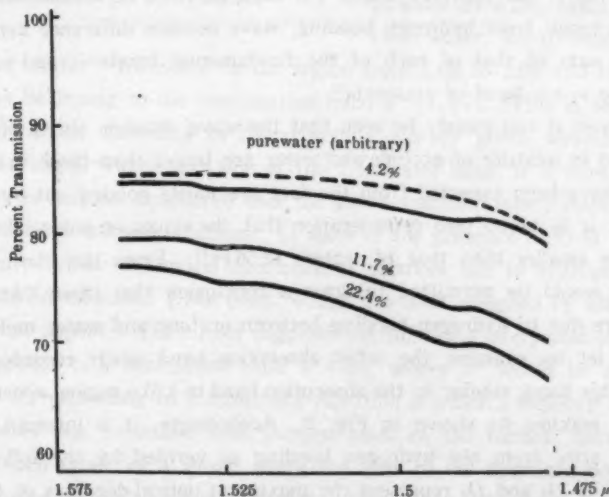


Fig. 1. Infrared absorption spectra of acetone-water mixtures in  $1.51\mu$  region. Cell thickness: 1.2 mm.

4) G. Herzberg: Infrared and Raman Spectra of Polyatomic molecules (D. Van Nostrand Company, Inc., New York, 1945), p. 281.

\* They were measured by the author at an extremely small concentration.

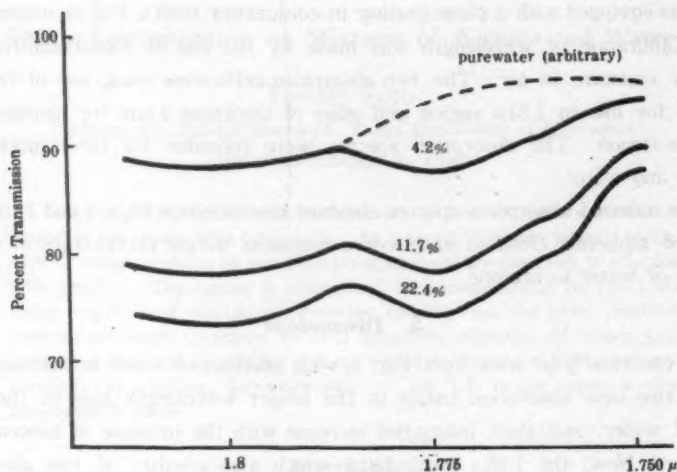


Fig. 2. Infrared absorption spectra of aceto-water mixtures in  $1.76\mu$  region. Cell thickness: 2 mm.

Referring to our previous results<sup>5)</sup>, it may therefore be considered that these two bands result from hydrogen bonding, wave number difference between them being the sum of that of each of the fundamental bands  $\nu_1$  and  $\nu_3$ , as is the case of the  $\nu_1 + \nu_2$  band of ammonia<sup>6)</sup>.

Moreover, it can clearly be seen that the wave number shifts of the  $1.38\mu$  water band in mixture of acetone and water are larger than those in water itself as might have been expected from the fact previously pointed out by the author et al.<sup>7)</sup>, if it is taken into consideration that the ionization potential of acetone,  $9.69\text{ eV}$ <sup>8)</sup>, is smaller than that of water,  $12.56\text{ eV}$ <sup>9)</sup>. From the above-mentioned results, it would be permitted to draw a conclusion that these two bands in question are due to hydrogen bonding between acetone and water molecules.

Next, let us examine the other absorption band newly recorded in  $1.76\mu$  region. This band, similar to the absorption band in  $1.51\mu$  region, consists of two absorption maxima as shown in Fig. 2. Accordingly, it is inferred that these two bands arise from the hydrogen bonding as verified by the following consideration. If  $D_1$  and  $D_2$  represent the maximum optical densities of the absorption bands observed in  $1.51\mu$  and  $1.76\mu$  regions respectively, they have the forms

5) Reference 4, p. 295. In the case of ammonia, owing to the symmetrical property, circumstance may be somewhat different from the present case.

6) K. Watanabe: J. Chem. Phys. **22** (1954) 1564.

7) J. D. Morrison and A. J. C. Nicholson: J. Chem. Phys. **20** (1952) 1221.

$$D_1 = k_1 C_1 l_1$$

and

$$D_2 = k_2 C_2 l_2$$

Here  $C_1$  and  $C_2$  are the concentrations of the absorbances from which two absorption bands result,  $k_1$  and  $k_2$  the extinction coefficients of these two bands,  $l_1$  and  $l_2$  the cell thicknesses used in the measurements of these two bands. Now, the values of the ratio  $D_1/D_2$ , calculated under the assumption  $C_1 = C_2^*$ , for three concentrations of water indicated in the figures, are in good agreement with one another within experimental error as listed in table 1.

Table 1. Ratios,  $D_1/D_2$ , of the maximum optical densities of the two absorption bands observed in  $1.51\mu$  and  $1.76\mu$  regions for three concentrations of water.

Weight-percentage of water to acetone	Maximum optical density ratio $D_1/D_2$
4.2	1.03 <sub>4</sub>
11.9	1.03 <sub>1</sub>
22.4	1.03 <sub>6</sub>

On the basis of these considerations, it is concluded that the bands observed in  $1.51\mu$  and  $1.76\mu$  regions are all due to the same absorbance, or, association compound. It cannot be considered that, in consequence of the hydrogen bonding, the bands in question have originated from the  $1.8\mu$  water band, which is the

only band of water\*\* measured in the region from  $1.6\mu$  to  $1.9\mu$  and interpreted by Ellis<sup>8)</sup> as belonging to the combination band  $\nu^* + \nu_1 + \nu_2$ . This is because the associational bands, according to the reasoning already given, should have appeared in the longer wavelength side of the  $1.8\mu$  water band, if it were the case.

However it may be considered that the above-described interpretation for the  $1.8\mu$  water band is incorrect, because, in spite of the presence of O-H stretching vibration  $\nu_1$ , no other absorption maximum or shoulder due to hydrogen bonding is found, and in addition,  $1.74\mu$  band, which has been assigned by Ellis to  $\nu^* + \nu_3 + \nu_2$ <sup>8)</sup> do not appear. The author suggests the following interpretation the  $1.8\mu$  band corresponds to a summation band  $\nu^* + 3\nu_3$ , where  $\nu^*$  would be allowed to consider as corresponding to a stretching vibration in which a molecule containing  $\nu_2$  and another one combined with oxygen atom of the former, oscillate with respect to each other as a group along the axis of the hydrogen bond, rather than interpreted as the torsional vibration. The reason, why such a combination

\* Generally speaking, it would not be conceivable that  $C_1$  is directly proportional to  $C_2$  in the concentration used in the present experiment.

\*\* The  $1.74\mu$  band, which has been interpreted to be  $\nu^* + \nu_3 + \nu_2$  by Ellis<sup>8)</sup>, was not observed in this experiment as described below.

8) J. W. Ellis: Phys. Rev. **38** (1931) 693.

band can appear and has comparatively large intensity, would clearly be explained by the following considerations: lone pair electrons which belong to the oxygen atom have large contribution to the dipole moment of the water molecule<sup>9)</sup>. The oscillation of the above-mentioned two molecules with respect to each other, owing to which the degree of delocalization of the lone pair electrons varies,<sup>10),11)</sup>, causing the dipole moment to vary and further in the normal vibration  $\nu_2$ , which belongs to the irreducible representation  $A_1$ , the dipole moment also varies along the symmetry axis. Therefore, when the dipole moment of the pair of the two molecules is expanded with respect to the normal coordinates for all possible vibrations of the molecules, the coefficient of the cross term of the two normal coordinates  $q_\mu$  and  $q_\nu$  corresponding to the vibrations in question,  $(\partial^2 M / \partial q_\mu \partial q_\nu)$ , is not zero and seems to be comparatively large. Of course, the mechanical anharmonicity of the vibrations must also be taken into consideration. Even with such interpretation, no absorption band corresponding to  $\nu^* + 3\nu_2$  would naturally appear in mixtures of acetone and water.

Also, it is scarcely conceivable that the bands in question occur by Fermi resonance between C-H stretching band and some combination or overtone band of acetone.

Recently, simultaneous vibrational transition has been studied by several investigators<sup>12),13),14)\*</sup>. Most probable interpretation for the cause of the associational bands, as is the case of the  $1.8\mu$  water band, seems to explain them as being due to simultaneous transition of O-H stretching band, C-O stretching band, and of any band associated directly with the hydrogen bonding, for example a band accompanying the vibration of each molecule as a group.

#### 4. Acknowledgment

The author wishes to express his sincere thanks to Professors Y. Fujioka and H. Ohtsuka for their deep interests and to Dr. S. Nagakura for his guidance and encouragement during the course of this work. Thanks are also due to Dr. M. Ogawa and Mr. H. Tsubomura for their kind discussions.

9) J. A. Pople: Proc. Roy. Soc. A, **202** (1950) 323.

10) K. Nukasawa, J. Tanaka and S. Nagakura: J. Phys. Soc. Japan **8** (1953) 792.

11) C. A. Coulson and U. Danielson: Ark. Fys. **8** (1954) 239, 245.

12) J. Jahrenfort and J. A. A. Ketelaar: J. Chem. Phys. **22** (1954) 1631.

13) J. A. A. Ketelaar and F. N. Hooge: J. Chem. Phys. **23** (1955) 749.

14) J. A. A. Ketelaar and F. N. Hooge: J. Chem. Phys. **23** (1955) 1549.

\* However, in these cases the intensity of the simultaneous transition is determined by the presence of terms such as  $(d\alpha/dq_i)_A(d\mu/dq_k)_B$  and  $(d\mu/dq_i)_A(d\alpha/dq_m)_B$ . (See reference 14).

## Effect of Iodic and Other Solutes on the Principal Water Band of the Raman Spectrum.

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As a complementary study of the structure of iodic acid molecules in solution, the present investigation reports the frequencies and intensities of the three components of the water band scattered in aq. solutions of iodic acid of concentrations ranging from 0.03N to 4.5N. The three frequencies  $\nu$  3213 (59.3), 3424 (65), and 3613 (36.5) observed in 0.03N sol., shift to 3353 (18.3), 3519 (22) and 3620 (18.2) respectively, when 4.5N solution is used, indicating a relative increase in the intensity of  $\nu$  3613 which is attributed to free  $H_2O$  molecules. The solute has been shown to cause a loosening and finally breaking up of hydrogen bonds uniting different  $H_2O$  molecules and as a result the number of free  $H_2O$  molecules increase, at the expense of the bonded ones to which  $\nu$  3213 and 3424 are attributed.

The effect of  $KCl \cdot HgCl_2$ ,  $2KCl \cdot HgCl_2$ ,  $2KBr \cdot HgCl_2$  etc. on the water band has also been studied and it is found that depolymerising action is more prominent with  $2KCl \cdot HgCl_2$  and  $2KBr \cdot CdBr_2$  than with  $KCl \cdot HgCl_2$  and  $HCl \cdot HgCl_2$ .

### 1. Introduction

In most of the physico-chemical measurements in aq. solutions, water is regarded as an inert solvent not influencing the properties of the solute, e.g. the conductivity of an electrolyte is made up of the sum of conductivity of the cation and the anion, which fact presumes that the solvent has no marked effect.

The idea is also universally accepted that binary electrolytes e.g. alkali halides show no Raman effect either in the solid, fused or dissolved condition, which has been taken as an evidence for the absence of a chemical or covalent bond in these compounds. Here the tacit assumption is also made that in the case of solution the solvent has no effect on the solute.

This, however, does not and should not mean that the solute does not effect the solvent. If water has a structure and a complicated one, it can, conveniently, be studied by means of Raman effect.

That the principal water band is, most probably, triplet in structure and that the three components lie near  $\nu$  3200, 3420 and 3610 and are influenced by

a change in temperature have been shown by a large number of workers, notably by I. R. Rao<sup>1)</sup>, Anantkrishnan<sup>2)</sup> and Cross, Burnham & Leighton<sup>3)</sup>. The effect of dissolved substances on the water band has been found to be similar to that of a rise in temperature viz. the intensity and maxima of the band are affected. According to C. S. Rao<sup>4)</sup>, substances like  $\text{HNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{H}_2\text{SO}_4$  etc. shift the maxima of the water band towards longer wavelength side and the band becomes sharper, while with  $\text{HCl}$  a reverse effect is observed after a certain concentration. I. R. Rao<sup>5)</sup> noticed a shift in the band as a whole towards longer wavelength with increasing concentration of  $\text{HNO}_3$ ,  $\text{NaNO}_3$  and  $\text{NaClO}_3$ . The effect of dissolved salts like chlorides and hydroxides on the water band has been investigated by Hibben<sup>6)</sup>, while Kujumzelis<sup>7)</sup> studied the effect of nitrates, chlorates, perchlorates etc. Some substances like acetone and pyridine do not appreciably affect the water band.

The present work was undertaken with the idea of systematically studying changes in the frequency and intensity of the three components of the water band as the concentration of iodic acid solution is increased from 0.3N to 4.5 N, and to find out whether iodic acid behaves like  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  or like  $\text{HCl}$  in respect of its action on the water band, although one is inclined to think that acids containing an O-H group, should show some similar behaviour towards the water band. The polymerised state of iodic acid may also lead to some interesting results.

The effect of the complex compounds of the mercuric chloride etc. on the water band is also studied. Remembering that water has a capacity to form hydrogen bonds, a probable explanation of the results observed is given.

## 2. Experimental

The investigation was carried out with the usual type of arrangement, the Fuess glass spectrograph being used for the purpose. The substances were Kahlbaum's purest chemicals. An iron arc comparison spectrum was photographed on each plate (Ilford H.P.). The microphotometric curve of the water band excited by  $\lambda$  4046.5 was obtained in each case and with its help the frequencies of the components of the water band were calculated.

- 1) Rao, I. R: Proc. Roy. Soc., **145A**, (1934) 489.
- 2) Anantkrishnan, R: Proc. Ind. Acad. Sci., **2A**, (1935) 296.
- 3) Cross, Burnham & Leighton: Jour. Am. Chem. Soc., **59**, (1937) 1134.
- 4) Rao, C. S: Ind. Jour. Phys., **9**, (1934) 195.
- 5) Rao, I. R: Proc. Roy. Soc., **130A**, (1931) 489.
- 6) Hibben: Jour. Chem. Phys., **5**, (1937) 166.
- 7) Kujumzelis: Zeits, F. Physik., **110**, (1938) 742.

For the determination of intensities, density-long (intensity) curve was drawn for the region  $\lambda$  3400 with the help of the intensity marks taken with varying slit-width, the source of illumination being tungsten filament lamp fed by a constant voltage. From this the intensity of each component is found out in terms of the slit-width, the corresponding density being given by the microphotometric curve. As the exposure of different plates were not quite proportional to the concentration used, the intensities given in the tables are not exactly absolute. Anyway, the relative intensities of the three components of a particular water band are quite reliable, and it is with this that we are more concerned with, than with the absolute values.

The horizontal and vertical components of the water band, were photographed simultaneously by interposing a suitably oriented double-image prism between the slit and the Raman tube. The values of  $\rho$  were calculated with the help of density-long (intensity) curve after allowing for various corrections necessary.

## 2. Results

Tables 1, 2, 3 give the Raman frequencies of the three components of the water band scattered in solutions of various concentrations and of different substances indicated. The intensities are shown in brackets. Table 4 shows the depolarisation factors ( $\rho$ ) of the three components of the water band observed in (1) 0.2N and (2) 4.5N  $\text{HIO}_3$  sol., the polarisation results of the Raman band of pure water, as observed by other workers, being added for comparison.

Table 1.  
Iodic Acid Solution

0.03N	0.07N	0.2N	1N	4.5N
3213 (59.3)	3290 (34)	3306 (23.9)	3346 (21.2)	3353 (18.3)
3424 (64.9)	3450 (43)	3458 (29.1)	3477 (24.9)	3519 (22)
3613 (36.5)	3613 (28.7)	3614 (20.5)	3615 (19.8)	3620 (18.2)

Table 2.

Kujumzelis		Author.		
$\text{NaNO}_3$	$\text{NaClO}_3$	$\text{HCl} \cdot \text{HgCl}_2$	$\text{KCl} \cdot \text{HgCl}_2$	$2\text{KBr} \cdot \text{HgCl}_2$
$(\text{NO}_3)'$	$(\text{ClO}_3)'$	$(\text{HgCl}_3)'$	$(\text{HgCl}_3)'$	
—	<i>no</i>	3277 (21.8)	3276 (16)	3243 (17.5)
3455 (?)	3465 (?)	3451 (26.6)	3450 (19.4)	3435 (22.3)
<i>no</i>	<i>no</i>	3580 (20.5)	3580 (15.3)	3607 (16.3)

Table 3.

Kujumzelis	Author.		
$\text{NaClO}_4$ ( $\text{ClO}_4$ )''	$2\text{HCl} \cdot \text{HgCl}_2$ ( $\text{HgCl}_4$ )''	$2\text{KCl} \cdot \text{HgCl}_2$ ( $\text{HgCl}_4$ )''	$2\text{KBr} \cdot \text{CdBr}_2$ ( $\text{CdBr}_4$ )''
3200 (like water)	3279 (22.4)	3280 (19.4)	3255 (17.5)
3420 (s)	3452 (30)	3453 (24.5)	3420 (21.7)
3580 (s)	3583 (22.7)	3582 (20.5)	3610 (18.3)

Table 4.

Deploration factors of the three components of the water band.

Component	Pure Water					Iodic Acid Sol.	
	Rama-swamy	Speechia	Cabannes & Rousset.	Cabannes & De Riols.	Anantkri-shnan.	Author.	
	1931	1932	1933	1934	1936	0.2N	4.5N
$\Delta\nu$ 3200	0.60	0.62	D	<0.3	0.12	0.27	0.76
3420	0.45	0.52	P	0.3	0.45	0.17	0.21
3610	0.54	0.54	—	P	0.80	0.29	0.57

### 3. Discussion

Meckes<sup>8)</sup> analysis of the vibration rotation spectrum of ordinary water-vapour led to the three normal frequencies for the monomeric  $\text{H}_2\text{O}$  molecule, viz  $\Delta\nu$  3759, 3670 and 1615. The third component of the observed principal water band viz  $\Delta\nu$  3613, which is nearly the same as that observed in the Raman spectrum of water vapour, lies near  $\Delta\nu$  3670. Thus, one of the three fundamental vibrations of the  $\text{H}_2\text{O}$  molecule is nearly  $\Delta\nu$  3610, while the same frequency as modified by coordination due to hydrogen bonds, probably appears as the remaining two frequencies of the water band viz. 3200 and 3420.

Whereas I. R. Rao<sup>9), 12)</sup> and C. S. Rao<sup>10)</sup> attribute  $\Delta\nu$  3200, 3420 and 3610 to the three discrete types of water molecules ( $\text{H}_2\text{O}$ )<sub>3</sub>, ( $\text{H}_2\text{O}$ )<sub>2</sub> and ( $\text{H}_2\text{O}$ ) respectively, Cross, Burnham & Leighton<sup>11)</sup> assign  $\Delta\nu$  3200 to a three-coordinated structure,  $\Delta\nu$  3420 to a two-coordinated structure while  $\Delta\nu$  3610 is attributed to free water molecules. The conception of polymerisation and that of coordination may, perhaps, be traced to the same origin viz. hydrogen bond.

8) Meckes: Phys. Seit., **XXX**, (1929) 907.

9) Rao, I. R.: Same as 1.

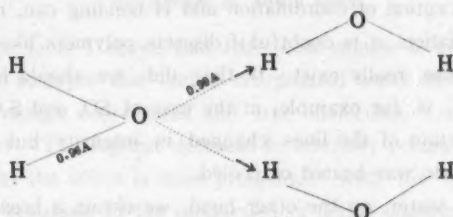
10) Rao, C. S.: Proc. Roy. Soc., **151A**, (1935) 507.

11) Cross, Burnham & Leighton: loc. cit.

12) Rao, I.R.: Proc. Roy. Soc., **145A**, (1934) 507.

#### 4. Structure of Water Molecule

Of all the structures proposed for an associated water molecule that given by Pauling<sup>13)</sup> seems to accord with experimental facts more fully. Pauling has shown that two of the four hydrogens which tetrahedrally surround a four-coordinated oxygen atom, are bonded to that oxygen, while the other two hydrogens are at greater distance from the oxygen and bonded to the other oxygen atoms as shown below:—



Pauling's view enables some interesting conclusions to be drawn. (1) If we take  $\Delta\nu$  3610 which is the frequency due to oscillation of a free O-H group in water (this being the same as (O-H) frequency observed in KOH etc.), we conclude that the number of such free groups should be very small, since this line is only weakly indicated in the microphotometric traces.

(2) According to Pauling the intermolecular vibrations of a co-ordinated water molecule could be represented as perturbed vibrations of the isolated water molecule. Such a perturbation arises from Hydrogen Bonds through the hydrogens of the molecule being considered. These H-bonds perturb only the O-H oscillator of which the hydrogen is involved in the hydrogen bond. It may be reasonable to assume that the amount of perturbation is a function of the distance of oxygen atom from the hydrogen of the O-H oscillator. We may, perhaps, go a little further and assume that, to a first approximation at least, the perturbation is inversely proportional to the square of the distance and so we have perturbed O-H frequency =  $3610 \times 0.96^2 / 0.99^2 = 3396$  or 3400 (nearly) which coincides with the most intense component of the water band. It is thus not unreasonable to attribute  $\Delta\nu$  3400 to an O-H frequency modified by a hydrogen bond.  $\Delta\nu$  3210 may be the result of a similar type of perturbation of the O-H frequency caused by, say, two hydrogen bonds.

While it is certain that some such process as H-bonding is responsible for the different kinds of vibrations of the O-H group, one may only in a qualitative

13) Pauling, L: Jour. Am. Chem. Soc., **57** (1935) 2680.

sense speak of three main types of molecules leading to shifts  $\Delta\nu$  3610, 3420 and 3210 which have been attributed to the three molecular species  $(\text{H}_2\text{O})$ ,  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ . X-ray evidence<sup>14)</sup>, in a sense, support the existence of polymers in liquid water. Water containing groups of three  $\text{H}_2\text{O}$  molecules bonded round a central  $\text{H}_2\text{O}$  molecule has been postulated on the basis of X-ray observations, and this would make the formula of the molecule  $(\text{H}_2\text{O})_4$ . Morgan & Warren<sup>15)</sup> speak of water as having a structure involving partial tetrahedral bonding, with continually changing neighbours.

While the conception of coordination and H-bonding can, in effect, give rise to a type of association, it is doubtful if discrete polymers like  $(\text{H}_2\text{O})_3$  and  $(\text{H}_2\text{O})_4$  in the chemical sense, really exist. If they did, we should have obtained unequivocal evidence, as, for example, in the case of  $\text{SO}_3$  and  $\text{S}_2\text{O}_6$ , Bhagvantam<sup>16)</sup> has shown that certain of the lines changed in intensity but not in frequency when sulphur-trioxide was heated or cooled.

In the case of water, on the other hand, we obtain a broad band with three maxima. If these maxima could be attributed to different definite molecular species, then under the influence of temperature or other factors which bring about a change in the proportion of these molecules, only the intensity should change *but not the frequency*. In our experiments, as well as in those reported by others, there is not only a change in the intensity of the maxima, but what is more important, there, is a shift of frequency also. The significance of the latter has been ignored in the explanation given on the hypothesis of polymers<sup>17)</sup>. Since the maxima observed undergo a continuous shift with external conditions, it is more rational to attribute them to molecules under different tensions produced by, say, H-bonding. The latter is easily susceptible to such factors as temp., presence of foreign substances, etc.

That an easily changing type of combination (H-Bond, coordination) is responsible for the water band, is further evidenced by I. R. Rao in a mixture of  $\text{H}_2\text{O} + \text{D}_2\text{O}$ <sup>18)</sup>. If water really consists of three types of molecules of thermal equilibrium, a substance like  $\text{D}_2\text{O}$  which, according to Rao, also consists of a similar equilibrium mixture and which in all other respects is exactly analogous to  $\text{H}_2\text{O}$ , surely cannot change its equilibrium. According to Rao's results the central maximum of pure water viz.  $\Delta\nu$  3443 has shifted to 3461 (i.e. by 18 units) by mixing with  $\text{D}_2\text{O}$ . This cannot be explained by a mere change in the

14) Katzoff: Jour. Chem. Phys., **2** (1934) 841.

15) Morgan & Warren: Jour. Chem. Phys., **6** (1938) 666.

16) Bhagvantam: Ind. Jour. Phys., **5** (1930) 49.

17) Rao, I. R. & Koteswaram, P: Ind. Jour. Phys., **12** (1938) 74.

18) Rao, I. R. & Rao, Y. P: Ind. Jour. Phys., **14** (1940) 139.

equilibrium composition of polymers.

We, therefore, attribute  $\Delta\nu$  3210 and 3420 to multiple and single coordinated water molecules respectively, instead of to  $(\text{H}_2\text{O})_3$  &  $(\text{H}_2\text{O})_2$ . The whole thing can better be explained in terms of coordination as this property is of a changing type while molecules like  $(\text{H}_2\text{O})_3$  &  $(\text{H}_2\text{O})_2$  chemically speaking, should have their frequencies unchanged under different conditions. The frequency  $\Delta\nu$  3610 is, of course, due to free water molecules.

#### 5. Effect of Iodic acid.

A reference to table 1 shows that Iodic acid causes a gradual loosening of the bond in the multiple and single coordinated water molecules, resulting in the production of single coordinated and free molecules, the latter being much greater in number. The highest decrease in intensity occurs in the component 3210, showing that the effect is most pronounced with the multiple coordinated water molecules, resulting in the production of single coordinated and free water molecules. The next highest decrease in the component  $\Delta\nu$  3420, shows that the effect in this case is even less pronounced than in the previous case. This is not unexpected since single coordinated water molecules can release only free  $\text{H}_2\text{O}$  molecules. The combined effect of the two processes is towards increasing the relative number of free  $\text{H}_2\text{O}$  molecules shown by the increased intensity of  $\Delta\nu$  3610.

#### 6. Shift in frequency.

Another significant fact in conformity with the above interpretation is with regard to frequency changes. It can be seen that there is a gradual increase in the frequency of  $\Delta\nu$  3210 and 3420, as the amount of solute is increased, the increase being highest in the first component. At 4.5N where the effect of solute is relatively greatest, the peak frequency  $\Delta\nu$  3420 corresponds more to that of  $\text{H}_2\text{O}$  (viz.  $\Delta\nu$  3610), than to any other, and the frequency  $\Delta\nu$  3210 due to multiple-coordinated water molecule, approaches the frequency corresponding to single coordinated water molecule. The component  $\Delta\nu$  3610, however, shows inappreciable increase in frequency as compared with the first two,—a fact which is significant though understandable.

If the coordinating H atom of the  $\text{H}_2\text{O}$  molecule associates with the O atom of the oxyacid  $\text{HIO}_3$  in preference to the O atom of another  $\text{H}_2\text{O}$  molecule, then this must result in the breaking up of the hydrogen bonds of the water molecule. In the Raman spectra this will show itself as a shift in the frequency, as is actually observed. The greater the amount of solute mixed, the more pronounced

ed are the structural changes brought about as a result of breaking of H-bonds. An increase in the shift of the maxima of the water band may be explained by assuming that the addition of solute results, by some mechanism, in the strengthening of the O-H bond by slowly weakening the corresponding H-bond, giving rise to this frequency.

The peak of the microphotometric curve becomes sharper as the concentration increases, which again points to the same thing.

### 7. Effect of other solutes.

Referring to table 2 it is seen that the order of intensities here is nearly the same as in pure water although there is some frequency shift. The results, as far as intensities are concerned, are comparable with those of Kujumzelis<sup>19</sup>, who reported the effect of  $\text{NO}_3^-$  &  $\text{ClO}_3^-$  ion on the water band. The structure of these ions is similar to that of  $\text{HgCl}_2$  with which we are probably, dealing here.

Coming to table 3 we notice a significant change, in that the intensity of  $\nu$  3582 is higher than that of  $\nu$  3279, showing that the depolymerising action is much more conspicuous here than in the previous case. It is likely that ions of the type  $\text{HgCl}_2$  or  $\text{CdBr}_2$  or as Kujumzelis has shown,  $\text{ClO}_4^-$  exert a similar action on the solvent.

### Depolarisation Factors:

Referring to table 4 it is seen that the results obtained for pure water, by different workers<sup>20-24</sup> vary to a great extent. The results of the author show that all the three components are polarised in a 0.2N as well as in a 4.5N sol., although there is a variation of the value of  $\rho$  as we pass on from the dilute to the concn. state.

Whether the variation of  $\rho$  is to be attributed to the variation in the geometric character of the oscillations involved, or has a bearing on the weakening of the H-bonds, due to solute, is rather difficult to decide, but it is certain that it has something to do with the structural changes involved.

In conclusion, the author wishes to express the gratitude to Dr. P. N. Sharma under whom the investigation was carried out. His grateful thanks are also due to late Mr. M. R. Nayar for his invaluable suggestions and for the keen interest he had taken during the course of the work.

19) Kujumzelis: loc. cit.

20) Ramaswamy, C: Nature., **127** (1931) 558.

21) Specchia: Cim., **9** (1932) 133.

22) Cabannes, J. & Rousset, A: Ann. De Pyhs., **19** (1933) 271.

23) Cabannes, J. & DeRiols, J: C.R., **198** (1934) 30.

24) Anantkrishnan, R: Proc. Ind. Acad. Sci., **3A** (1936) 201.

## Raman Effect and Constitution of Potassium Thiocyanate

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The Raman spectra of Aqueous solutions of KCNS and  $\text{NH}_4\text{CNS}$  as observed by Fuess glass spectrograph, show three Raman lines at about  $\Delta\nu$  2067, 760 and 499. The polarisation measurements show all the lines to be polarised. A bent unsymmetrical structure for the thiocyanate ion is therefore suggested.

### 1. Introduction

The Raman spectrum of the thiocyanate ion has formed the subject of investigation by a number of workers. Pal and Sen Gupta<sup>1)</sup> reported two lines at  $\Delta\nu$  2067 and 745 for the KCNS solution, while the same two frequency shifts were observed, in the crystalline state, by Krishnamurti<sup>2)</sup>. Kondratev and Setkina (1936) have investigated KCNS<sub>2</sub> and obtained two frequencies at  $\Delta\nu$  2051 and 575.

The thiocyanate ion  $(\text{SCN})^-$  may belong to the linear type ABC having the symmetry  $C_{\infty v}$  which should theoretically yield three fundamental Raman frequencies of which two are polarised and one depolarised. Alternatively, the ion may have an unsymmetrical bent structure ( $C_2$ ) which again should give three Raman lines of which all are polarised and none depolarised. It is thus clear that mere number of Raman lines obtainable for the SCN ion will not help us in deciding between the two types of structures. The crucial test will be the measurement of the state of polarisation of the Raman lines for the ion.

While Langseth, Nielson and Sorensen<sup>3)</sup> report some general similarity between the Raman spectra of COS, SCN and ClCN and are in favour of the linear type for the SCN ion, the results quoted by Hibben<sup>4)</sup> for polarisation measurements for the ion, go against such an interpretation. Moreover either structure should theoretically give three Raman lines whereas only two have so far been reported.

The present paper concerns itself with a microphotometric examination of the Raman spectrum of potassium thiocyanate in solution. Raman spectrum of

1) Pal and Sen Gupta: *Ind. Jr. Phys.*, **5** (1930) 13.

2) Krishnamurti: *Ibid.*, **5** (1930) 651.

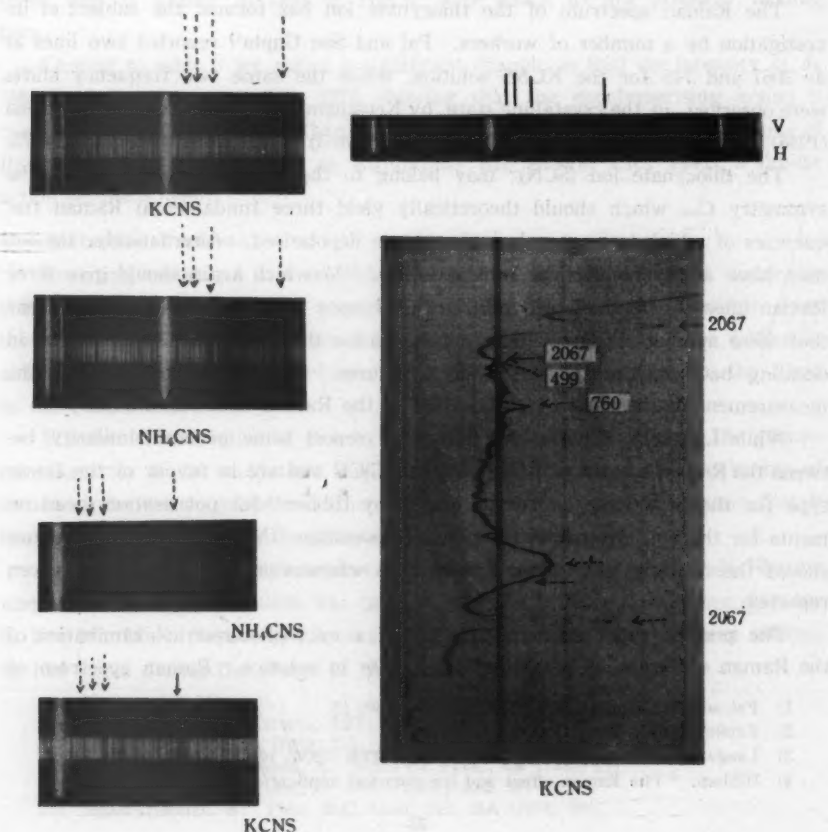
3) Langseth and others: *Z. Physik. Chem.*, **27B** (1934) 100.

4) Hibben: "The Raman effect and its chemical applications" (1939).

Ammonium thiocyanate has also been photographed for comparison. After keeping these two for about a fortnight, they were again experimented upon to study changes, if any, due to hydrolysis. A polarisation picture for the thiocyanate ion has also been photographed. The results so obtained, supplemented by polarisation results, have been discussed in relation to the structure of the thiocyanate ion.

## 2. Experimental

The substances used were Kahlbaum's pure chemicals further purified by repeated slow crystallisation. The arrangement for photographing the Raman spectra was the usual one, Fuess glass spectrograph being used for the purpose. The exciting radiations were  $\lambda 4046.5$ ,  $\lambda 4078$  and  $\lambda 4358.34$  of the mercury arc. The Raman lines were measured by means of Hilger L 13 micrometer in com-



parison with an iron arc spectrum.

As some of the lines are rather broad, a microphotometric record of the Raman lines of KCNS was also taken to locate points of maximum intensity and to resolve them into components, if any. To measure the depolarisation factor  $\rho$  of the Raman lines, horizontal and the vertical components were photographed simultaneously by interposing a suitably oriented double-image prism in the track of scattered light. Suitable correction was applied to the observed value of the depolarisation factor by finding out the value of  $\rho$  for carbon-tetrachloride. Exact evaluation of the value for depolarisation factor was possible only for the relatively stronger line  $\lambda\nu$  2067. The other two lines are weak and were visually found to be polarised.

### 3. Results

The results of the investigation are tabulated in the accompanying table, the results obtained by other main workers being shown side by side. The letter  $\rho$  stands for polarised while the numbers in brackets represent the relative intensities of the lines as estimated from the microphotograph.

Table 1. KCNS solution (aq)—40%. Exposure—40 hours.  
Raman frequencies in  $\text{cm}^{-1}$ . Frequencies of fresh solution measured with the help of microphotograph.

Exciting radiation	Pal and Sen Gupta.	Langseth and others	Author		
			Fresh	Solution after a fortnight	State of Polarisation
$\lambda$ 4358.34	2067	2056.6	2067.0 (10)	2064.2	0.55
"	—	796	—	—	—
"	745	750.4	760.4 (1.5)	758.3	P
"	—	—	499.0 (0.5)	—	—
4078	—	—	2066.8 (0.5)	2069.2	P
4046.5	2064	—	2067.9 (7)	2065.7	0.53
"	741	—	—	—	—

Table 2.  $\text{NH}_4\text{CNS}$  solution (aq)—28%. Exposure—30 hours

Exciting radiation	Pal and Sen Gupta	Langseth and others	Author	
			Fresh	Solution after a fortnight
$\lambda$ 4358.34	2067	2056.6	2061.4	2063.8
		796		
		750.4	759.6	759.7
4078	—	—	2065	2063.0
4046.5	2067	—	2064	2062.8

#### 4. Description of results

The Raman line at  $\Delta\nu$  2067 is the broadest and most intense covering a width of about  $40\text{ cm}^{-1}$ . It consists of a *single* component as shown by the microphotograph, and is excited separately by  $\lambda$  4358,  $\lambda$  4046 and  $\lambda$  4078. The line at  $\Delta\nu$  760 is fairly sharp though weak. The line excited by  $\lambda$  4078 appears as a weak broad diffuse band is of some interest and needs some discussion.

At first sight one is inclined to think that the diffuse band referred to above should represent only the line  $\Delta\nu$  2067 excited by the weak mercury line  $\lambda$  4078. If it is so, the microphotograph should show, like  $\Delta\nu$  2067 excited by  $\lambda$  4358, a single component of that shift. But actually we find from the microphotograph of the Raman spectrum of KCNS (fresh) that the band, instead of showing a sharp peak, consists of two close components. In fact, the band includes not only the highest Raman shift 2066.8 due to weaker exciting radiation  $\lambda$  4078 but has, in addition, a close companion at about  $\Delta\nu$  499, due to the exciting radiation  $\lambda$  4358.34. Although the microphotograph of Raman spectrum of  $\text{NH}_4\text{CNS}$  solution could not be taken, yet considering the width of the band, a line at  $\Delta\nu$  499 is likely to be present there also.

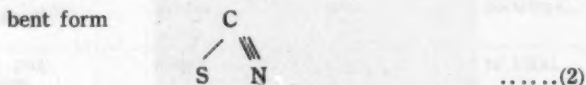
It appears that none of the previous workers tried to measure the line excited by  $\lambda$  4078. The situation can well be clarified by using a filter which would suppress the  $\lambda$  4046 group of lines and then photographing the Raman spectrum of the solution.

The depolarisation factor  $\rho$  for the strongest line  $\Delta\nu$  2067 is found to be 0.55 and is therefore polarised. The other two lines which are weak are seen to be polarised from the photograph.

#### 5. Discussion of the structure of $\text{SCN}^-$ ion

It is thus seen that in addition to the two lines observed by previous workers a new line at  $\Delta\nu$  499 for the  $\text{SCN}^-$  ion has been observed for the first time by the author so that the  $\text{SCN}^-$  ion shows three Raman lines as predicated theoretically.

For the thiocyanate ion the two probable structures are:—



Langseth and others have compared the spectra obtained from COS, CICN and  $\text{SCN}^-$ . They are supposed to have similar structure each giving three fundamental Raman frequencies as given below:—

	COS	CICN	SCN <sup>-</sup>
$\nu_3$	2055	2201	2067
$\nu_1$	859	729	767
$\nu_2$	524	397	499 (author)

It seems quite probable that like COS and CICN, SCN<sup>-</sup> ion may also belong to the linear type ABC and as such should give three Raman lines  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  of which  $\nu_2 + \nu_1$  should be polarised and  $\nu_3$  depolarised. They report a weak band at  $\Delta\nu$  796 which they call  $2\nu_2$  so that  $\nu_2$  is 398. The author in spite of the most searching investigation has failed to record a band at  $\Delta\nu$  796. There is however a microphotometric evidence of the presence of a weak line at  $\Delta\nu$  499 which may be called  $\nu_2$ .

The contention of Lagseth and others that SCN<sup>-</sup> ion has a linear structure, is belied by the polarisation results obtained by the author which show all the lines to be polarised and none depolarised to the limit. This observation is supported by Hibben according to whom  $\Delta\nu$  720 has  $\rho=0.08$  and  $\Delta\nu$  2066 has  $\rho=0.37$  meaning thereby that both the lines are polarised. The very fact that  $\Delta\nu$  2066 is not depolarised goes to show that the SCN<sup>-</sup> ion has a bent structure as shown by structure (2) above.

The X-ray studies of KCNS made by Bussem, Gunther and Tubin<sup>5)</sup> are in favour of the bent structure, the bonded angle being about 127°.

### 6. Interpretation of frequencies

$\Delta\nu$  2067:—The C=N characteristic frequency in the non-cyclic compounds is near  $\Delta\nu$  1640. In the present case the frequency observed for the cyanide group is  $\Delta\nu$  2067 which is greater than that represented for C=N. This means that  $\Delta\nu$  2067 must be attributed to C≡N group. It may also be noted that a frequency near  $\Delta\nu$  2067 is exhibited by many cyanogen compounds such as KCN, KCNO, K<sub>2</sub>Hg CN<sub>4</sub> and KAg (CN)<sub>2</sub> in all of which the existence of the triple bonded C≡N group is assumed.

$\Delta\nu$  760:

C-S shift in mercaptans and thioethers occurs near  $\Delta\nu$  650 and 733 and so it is concluded that  $\Delta\nu$  760 observed with the SCN<sup>-</sup> ion corresponds to the S-C vibration and not to S=C vibration for which the frequency should be  $\Delta\nu$  1050.

$\Delta\nu$  499:

This may be attributed to the S atom vibrating against the CN group as a whole.

5) Bussem, Gunther and Tubin: Z. Physik. Chem., **24B** (1934) 1.

The presence of a triple bond frequency of CN group and single bond frequency of S-C group eliminates the possibility of the form  $S=C=N$ , and the most probable structure for the SCN ion is the bent unsymmetrical one with the symmetry  $C_s$ . Lastly a fortnight old solution was found to show no appreciable change in the Raman spectrum of the ion.

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